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1,4-Diazoniabicyclo[2.2.2]octane aqua-bis(oxalato-κ^2O,O')copper(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 167 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.103
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_6H_{14}N_2)[Cu(C_2O_4)_2(H_2O)]\cdot 2H_2O$, crystallizes in the space group $P\overline{1}$. In the solid state, the $[Cu(ox)_2(H_2O)]^{2-}$ units (ox is oxalate, C_2O_4) dimerize to give a tetragonally distorted CuO_6 coordination environment. Extensive hydrogen bonding between the oxalate, the coordinated water, the 1,4-diazoniabicyclo[2.2.2]octane dications ($[dabcoH_2]^{2+}$) and the water of crystallization determines the crystal packing.

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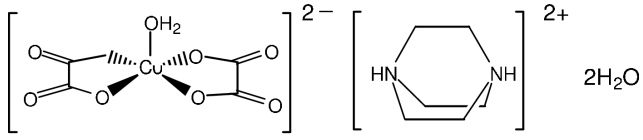
Comment

Blue crystals of the title compound, (I), were obtained by a slow diffusion technique in an aqueous gel. This ionic compound crystallizes in the triclinic space group $P\overline{1}$, with two formula units per unit cell. The structure of (I) contains $[Cu(ox)_2(H_2O)]^{2-}$ (ox is oxalate, C_2O_4) units, in which the Cu^{II} ion is coordinated by two chelating oxalate ions in a planar geometry, and the coordinated water molecule forms a long axial contact [Cu1—O1*W* 2.344 (7) Å]. These units dimerize through one of the coordinating O atoms of the oxalate (Fig. 1 and Table 1), resulting in a Cu1···Cu1^{i} separation of 3.818 (8) Å [symmetry code: (i) $-x, 1-y, 1-z$]. The long Cu1—O3^{i} contact of 2.906 (10) Å gives an idea of the weakness of the dimerization interaction.



(I)

The number of hydrogen-bond acceptor sites in (I) is greater than the number of potential hydrogen-bond donating groups. We note that all D—H groups are involved in hydrogen bonding, and that there are seven different (near) linear and one bifurcated hydrogen-bond interactions (Table 2). Neighbouring $[Cu(ox)_2(H_2O)]_2^{4-}$ units are directly hydrogen-bonded into chains. These chains are hydrogen-bonded through the water of crystallization, resulting in an extensive three-dimensional network (Fig. 2). The unsymmetric bifurcated hydrogen bond between the oxalate and 1,4-diazoniabicyclo[2.2.2]octane ($[dabcoH_2]^{2+}$) is a motif seen in almost all other compounds containing $[dabcoH_2]^{2+}$ and ox^{2-} (Vaidhyanathan *et al.*, 2001; Lee & Wang, 1999; Malfant *et al.*, 1990), although we note that this hydrogen-bonding pattern is not uncommon in oxalate compounds.

As described previously (Keene *et al.*, 2003, 2004), discrete mono- and dinuclear metal oxalate species may be formed

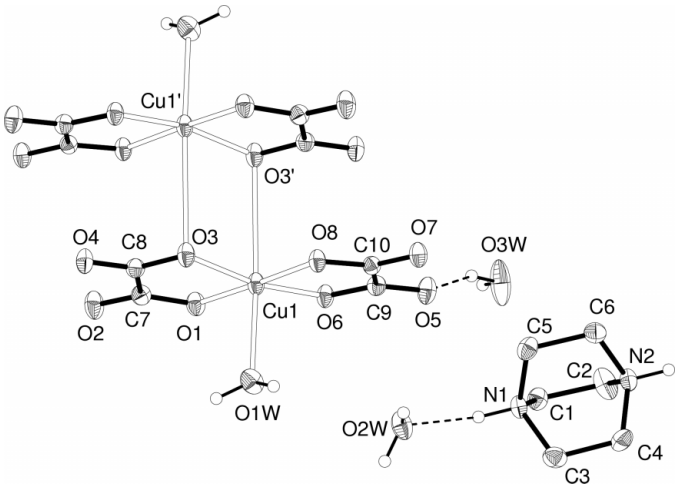


Figure 1
The asymmetric unit and selected symmetry equivalents of (I), showing the dimerization of the $[Cu(ox)_2(H_2O)]^{2-}$ unit. Displacement ellipsoids are drawn at the 50% probability level. Some H atoms have been omitted for clarity. Primed atoms are generated by the symmetry operation $(-x, 1-y, 1-z)$.

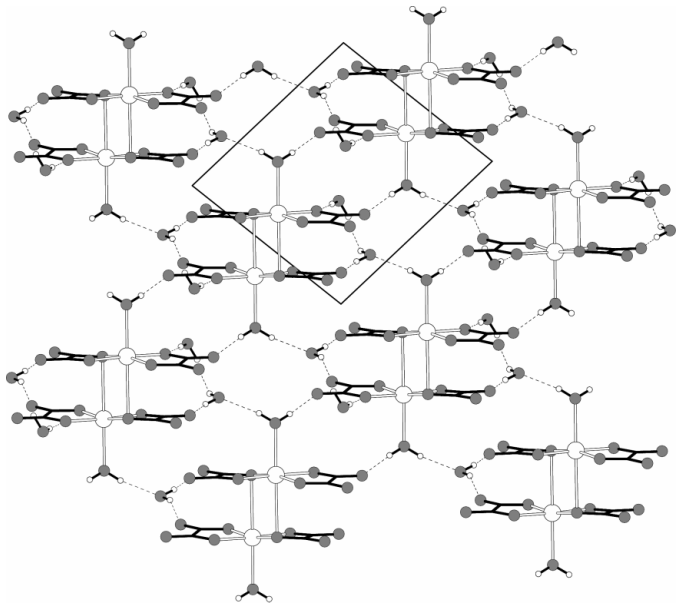


Figure 2
Hydrogen-bonding interactions (dashed lines) between $[Cu(ox)_2(H_2O)]_2^{4-}$ clusters and the water of crystallization, viewed along the *b* axis.

when the bridging potential of the oxalate is reduced. This can be achieved either through the use of capping ligands or by a high concentration of the oxalate dianion, in both cases resulting in coordinatively saturated complexes. The large Jahn–Teller effect in Cu^{II} makes the structural chemistry of copper oxalate compounds different from that of other 3*d* transition metals. In particular, a displacement of the labile axial water molecules during crystallization is commonly observed, and a polycatenation process results in chains of $[Cu(ox)_2]_2^{2n-}$ in the solid state. Very few examples of isolated $[Cu(ox)_2(H_2O)_2]^{2-}$ (Insausti *et al.*, 1994; Keene *et al.*, 2004) or dimerized species (Savel'eva *et al.*, 1992) have been observed in the solid state. In the case of (I), the extensive hydrogen-bonded network stabilizes the discrete dimerization of the copper bisoxalate dianions, to give isolated $[Cu(ox)_2(H_2O)]_2^{4-}$ units.

Experimental

Single crystals of (I) were synthesized by a gel-crystallization technique. $CuSO_4{\cdot}5H_2O$ (100 mg, 0.40 mmol) was dissolved in distilled water (18 ml). Tetramethoxysilane (2 ml) was added and the mixture stirred until monophasic, then allowed to set in a test tube. A solution of 1,4-diazoniabicyclo[2.2.2]octane bis(hydrogenoxalate) (200 mg, 0.68 mmol) was added to the top of the gel. After two weeks, light-blue crystals of (I) had formed in the gel. IR (KBr, diffuse reflectance, cm^{-1}): 3450 *s* (O—H stretch), 2823 *s* (C—H stretch), 2650 *s* (N—H stretch), 1681 *s* and 1658 *s* (oxalate), 1412 *s* (oxalate), 1291 *s*, 1059 *s*, 850 *s*, 801 *s*, 607 *m*, 540 *m*, 495 *m*; UV/VIS/NIR (diffuse reflectance, cm^{-1}): 14 400 (*d*-*d*), 35 700 (oxalate).

Crystal data

$(C_6H_{14}N_2)[Cu(C_2O_4)_2(H_2O)]{\cdot}2H_2O$	$Z = 2$
$M_r = 407.82$	$D_x = 1.793$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 9.3847$ (7) Å	Cell parameters from 9717 reflections
$b = 9.4884$ (6) Å	$\theta = 2.9$–27.5°
$c = 9.6936$ (5) Å	$\mu = 1.51$ mm^{-1}
$\alpha = 62.150$ (4)°	$T = 167$ (2) K
$\beta = 81.987$ (4)°	Block, blue
$\gamma = 87.868$ (3)°	0.42 × 0.12 × 0.08 mm
$V = 755.36$ (9) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	3465 independent reflections
φ and ω scans	3018 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)	$R_{int} = 0.060$
$T_{min} = 0.696$, $T_{max} = 0.886$	$\theta_{max} = 27.6^\circ$
7866 measured reflections	$h = -10 \rightarrow 12$
	$k = -12 \rightarrow 12$
	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.8532P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.103$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.71$ e Å^{-3}
3465 reflections	
241 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O6	1.9366 (18)	Cu1—O1	1.9584 (18)
Cu1—O3	1.9458 (19)	Cu1—O8	1.9617 (17)
Cu1—O3^{i}	2.9058 (18)	Cu1—O1*W*	2.343 (2)

Symmetry code: (i) $-x, 1-y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2W	0.91	1.84	2.698 (4)	157
N2—H2···O4^{ii}	0.91	1.90	2.690 (3)	144
N2—H2···O2^{ii}	0.91	2.28	2.978 (5)	133
O2W—H21···O8^{iii}	0.87 (2)	1.95 (2)	2.819 (5)	178 (2)
O2W—H22···O3W^{iv}	0.87 (2)	2.36 (2)	3.201 (4)	163 (2)
O3W—H31···O5	0.88 (4)	1.95 (4)	2.770 (6)	155 (4)
O1W—H11···O7^{iii}	0.87 (3)	1.98 (3)	2.837 (5)	169 (3)
O1W—H12···O3W^{v}	0.875 (18)	1.942 (19)	2.800 (6)	166.1 (16)
O3W—H32···O2^{vi}	0.87 (3)	1.88 (3)	2.703 (6)	157 (3)

Symmetry codes: (ii) $1+x, y, 1+z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 2-y, 1-z$; (v) $x, y, z-1$; (vi) $-x, 2-y, 1-z$.

H atoms bound to C and N atoms were positioned geometrically and refined as riding, with C—H = 0.97 and N—H = 0.91 Å, and with U_{iso}(H) = 1.2U_{eq}(parent atom). H atoms bound to O atoms were located in difference maps, but their distances and angles were restrained to literature values.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT* (Nonius, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) in *WinGX*; molecular graphics: *DIAMOND* (Brandenburg, 1999).

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